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This report summarizes activities related to ONR grant N00014-97-1-0879 to the Georgia Tech Research Corporation, for the period 1 June 1997 through September 30 1997 (Phase I). The work during Phase I has focused on (1) a sensitivity analysis of the effects of irrigation on the biogeochemistry of coastal marine sediments, 2) the upgrading of the existing multicomponent reactive transport model for early diagenesis, and (3) the preliminary development of a stochastic algorithm to represent burrowing activities of benthic macrofauna.

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Quantitative Chemical Mass Transfer in Coastal Sediments during Early Diagenesis

Effects of Biological Transport, Mineralogy, and Fabric

FINAL REPORT

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INTRODUCTION

This report summarizes activities related to ONR grant N00014-97-1-0879 to the Georgia Tech Research Corporation, for the period 1 June 1997 through September 30 1997 (Phase I). The work during Phase I has focused on (1) a sensitivity analysis of the effects of irrigation on the biogeochemistry of coastal marine sediments, 2) the upgrading of the existing multicomponent reactive transport model for early diagenesis, and (3) the preliminary development of a stochastic algorithm to represent burrowing activities of benthic macrofauna.

ACHIEVEMENTS

Reactive transport code

The basis for the modeling efforts is STEADYSED1, a multi-component reactive transport code for steady-state early diagenesis which fully incorporates the reaction couplings among the reactive species of C, O, N, S, Fe and Mn. The model has been tested against extensive data sets collected by Canfield *et al.* (1993a, b) at three coastal marine sites that exhibit high rates of combined iron and manganese (hydr)oxide reduction. Results show that the model provides a consistent explanation of the entire body of multi-component, multi-site observations. The measured concentration profiles of 28 individual pore water and solid sediment species are satisfactorily reproduced. Furthermore, the model predicts the observed distributions of sulfate reduction rates, as well as diagnostic features of the pore water pH profiles.

The coupled nature of the reactive species distributions constrains the values of reaction and transport parameters, because a single set of parameters must account for the distributions of all the species at a given site. The parameters are further separated into site-dependent (e.g., deposition fluxes, bottom water composition, mixing coefficient, porosity) and reaction-specific parameters (e.g., rate coefficients, apparent equilibrium constants, limiting substrate concentrations). When fitting model-calculated distributions to observed ones, care is taken to minimize variations of the reaction-specific parameters from one site to another. This modeling strategy emphasizes extraction of reaction parameters from field data that are mechanistically meaningful.

Effects of irrigation

A sensitivity analysis was performed with STEADYSED1, under boundary conditions representative of coastal marine depositional environments. Conditions were chosen on the basis of previous work (Van Cappellen et al., 1993; Tromp et al., 1995; Middelburg et al., 1997). The results show that model-calculated benthic exchange fluxes of most solutes are dominated by irrigation. Because of high rates of molecular oxygen reduction in organic-rich coastal sediments, the contribution of molecular diffusion to benthic uptake of O_2 may in some cases be of the same order of magnitude or even larger than that of irrigation. For nitrate,

molecular diffusion and irrigation cause exchange fluxes in opposite directions. As a consequence, there is a net transfer of nitrate from the water column to the sediments, although the interfacial pore water gradients predict diffusional fluxes out of the sediments. The results highlight the fundamental importance of pore water irrigation by macrofauna in controlling solute exchanges between sediments and water column in coastal environments.

Benthic fluxes and chemical conditions in sediments not only depend on the integrated intensity of irrigation, but also on the depth distribution of the irrigation exchange coefficient. This is shown in Figure 1, where three different distributions of the vertical irrigation exchange coefficient, α (in units of yr^{-1}), are considered. In two cases (1 & 3), the irrigation coefficient is assumed to decay exponentially with depth. This is the distribution used, for example, by Martin and Banta (1992) to reproduce tracer distributions of pore water bromide and $^{222}Rn / ^{226}Ra$ disequilibrium in Buzzards Bay, Massachusetts. In the other case (2), the depth distribution of α follows a step function, that is, a uniformly irrigated surface layer overlies non-irrigated sediment. The depth integral of α is the same for all three distributions. Thus, the simulations compare sediments experiencing the same overall irrigation intensity.

The calculated pH profiles show distinct differences between the three irrigation scenarios (Figure 1). (Note: pH is one of the most sensitive parameters of sediment biogeochemistry.) The differences are most pronounced when comparing the step function to the exponential distributions. In the depth range 2-3 cm, the predicted pH values may deviate from one another by as much as one pH unit, i. e. the equivalent of an order of magnitude in hydrogen ion concentration.

Figure 1. Irrigation scenarios: (a) imposed depth distributions of the irrigation exchange coefficient; (b) calculated pH distributions. Calculations were performed under conditions typical of a coastal marine sediment. Boundary conditions and parameter values are the same in the three simulations, except for the distribution of the irrigation exchange coefficient. See text for further discussion.
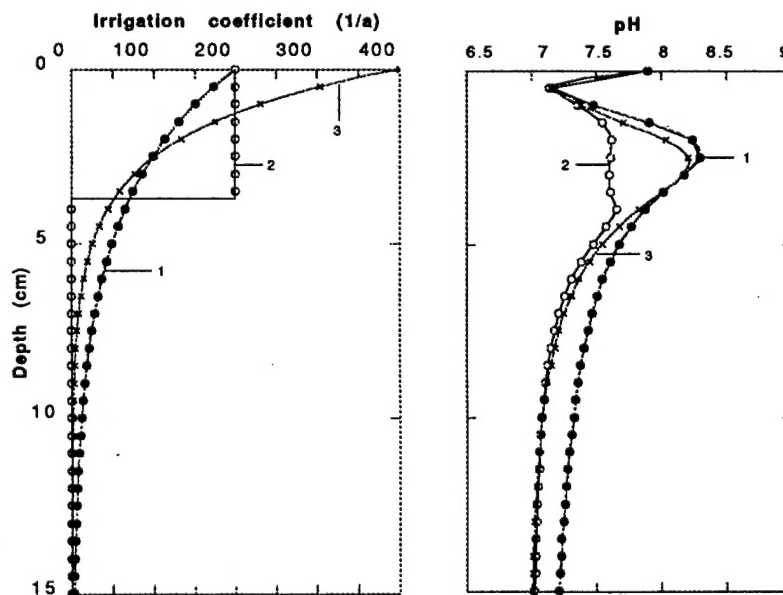
Existing early diagenetic models use idealized depth distributions of the irrigation coefficient such as those presented in Figure 1. Nonetheless, little data or theoretical arguments have been presented for selecting one distribution over another (for exceptions, see: Martin and Banta, 1992; Wang and Van Cappellen, 1996). The sensitivity analysis performed here, however, shows that the depth distribution of the exchange coefficient has a significant impact on sediment biogeochemistry. A large part of the work planned for Phase II of the project will be devoted to the development of better theoretical and experimental constraints on the functional dependence of α on depth below the water-sediment interface.

CaCO₃ and pH buffering

Dissolution of deposited biogenic $CaCO_3$ or precipitation of authigenic $CaCO_3$ may exert a critical control on pore water pH, alkalinity and total dissolved inorganic carbon (e.g., Gaillard et al., 1989; Cai et al., 1995). The published version of STEADYSED1 (version 1.1) does not include the dissolution and precipitation reactions of $CaCO_3$. In the absence of buffering by these reactions, the model simulations tend to overpredict the magnitude of pore water pH fluctuations.

STEADYSED1 was upgraded (version 1.2) by including the rates of $CaCO_3$ dissolution and precipitation in the continuity equations of Ca^{2+}, $CaCO_3$, total inorganic carbon (TC) and total alkalinity (Alk). As before, the pH profile is calculated by assuming that the dissolved carbonate system remains in local equilibrium. This is justified by the fast homogeneous acid-base kinetics. Several rate models for $CaCO_3$ are available for the user to choose from, as summarized in Table 1. Preliminary results show that by explicitly including $CaCO_3$ dissolution, the pore waters are buffered against large decreases in pH. More simulations are needed to fully assess the effects of $CaCO_3$ precipitation.

Table: Options for $CaCO_3$ dissolution/precipitation kinetics in Steadysed1 (v. 1.2)

Model	Rate expression	Reference
Empirical	$R_d = k_d[CaCO_3](1-\Omega)^{4.5}$ $R_p = k_p(\Omega-1)^{2..2}$	R_d: Cai et al. (1995) R_p: Zhong and Mucci (1993)
Mechanistic I	$R_d = k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3$ $R_p = k_{-1}a_{Ca^{2+}}a_{HCO_3^-} + k_{-2}a_{Ca^{2+}}a_{HCO_3^-}^2 + k_{-3}a_{Ca^{2+}}a_{HCO_3^-}$	Chou et al. (1989)
Mechanistic II	$R_{total} = k_1[H^+] + k_2[H_2CO_3^0] + k_3[H_2O] - k_4[Ca^{2+}][HCO_3^-]$	Plummer et al. (1979)
Mechanistic III (surface reaction)	$R_{total} = k_1 > CO_3^- a_{H^+}^2 + (k_2 - k_5) > Ca^+ a_{H_2CO_3} + k_4 - (k_6 - k_3) > CO_3H^0 a_{CaHCO_3^+} - k_7 > Ca^+ a_{H_2CO_3} a_{CaCO_3^0} - k_8 a_{CaCO_3^0}$	Arakaki and Mucci (1995)

R_d: dissolution rate; R_p: precipitation rate; R_{total}: overall reaction rate; a_i: activity of solute i; $[i]$: concentration of solute i; k_i: rate constant; $>i$: density of surface species i

The new version of the reactive transport code has not yet been made publicly available because some numerical problems remain to be solved. These problems are the consequence of the fast rates of $CaCO_3$ dissolution and precipitation, relative to the other kinetic processes represented in the model (e.g., the degradation of organic matter). Large differences among rate terms in the continuity equations are prone to cause numerical instabilities in the finite difference solutions. We are currently implementing changes in the code that counter these instabilities.

Stochastic burrowing

First steps have been taken in the development of a two-dimensional (2-D) stochastic model for random vertical burrowing. In this model the water-sediment interface is represented by a set of equally spaced spatial nodes. The algorithm considers each node in succession and decides whether or not to initiate burrowing. The decision is based on a randomly selected number, whereby the relative range of values leading to burrowing is determined by the average normalized burrow density.

The burrowing strategy plus environmental constraints that direct the activity of the macrofauna are translated into a probability distribution for the burrow length. Once a node has been selected as the site of a burrow, the length is determined by generating another random number. The value ranges assigned to different lengths are proportional to the corresponding probabilities. Based on numerous realizations of the stochastic burrow model, we calculate the average depth distribution of available burrow surface area (a proxy for the exchange coefficient), plus the deviation from the average. In this manner a statistical, rather than a deterministic, description of sediment burrowing is achieved. Our efforts in the near future will focus on the formulation of realistic probability distributions for burrow depths.

OTHER ACTIVITIES

A meeting of the P.I.s and the Program Officer was held at the Naval Research Laboratory in Stennis on September 26, 1997. Progress to date by the different laboratories was reviewed, and plans for Phase II (12/1/97 to 9/30/99) were discussed. Emphasis was placed on strengthening the integration of the P.I.s' efforts.

Work has begun on a manuscript on the effects of bio-irrigation on solute exchanges using data from the June 97 cruise to the Dry Tortugas organized by NRL (Lavoie, chief scientist). Dr. Furukawa is the lead author of this collaborative effort.

An abstract based on research closely related to that supported by this grant was submitted to the special session on *Diagenesis in Coastal and Marginal Sediments* of the 1998 Ocean Sciences Meeting (San Diego, February 9-13, 1998). It is entitled "*Spatial and Temporal Variability of the Iron and Sulfur Cycles in Salt*

Marsh Sediments: An Integrated Geochemical and Microbiological Study", by P. Van Cappellen, A. Roychoudhury, E. Viollier, K. Lowe, T. DiChristina, T. and J. Kostka.

The following activities are in the planning stage; they will enhance the visibility of research activities supported by ONR grant N00014-97-1-0879.

- A series of invited lectures by the P. I. at the Graduate College of GEOMAR (Forschungszentrum für marine Geowissenschaften) in Kiel, Germany (Nov. 26-28, 1997). The lectures will focus on the theoretical, numerical and experimental aspects of reactive transport in marine sediments.

- The organization by the P. I. of a thematic session entitled *"Biogeochemical Dynamics: From Molecular Approaches to Predictive Models"* at the Conference on Southeast Coastal Ocean Research (SECOR) (Savannah, April 7-10, 1998).

PERSONNEL

In addition to the P. I., first-year graduate student Chao Liu and Postdoctoral Fellow Eric Viollier have been involved in upgrading the STEADYSED1 code and running sensitivity simulations. Meanwhile Dr. Viollier's appointment at Georgia Tech has ended. In anticipation of continued funding for Phase II of the project, a new Postdoctoral fellow has been recruited to work on the stochastic bio-irrigation model: Dr. Carla Koretsky (Ph. D. 1997, Johns Hopkins University) will join the P.I.'s research group on January 1, 1998.

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